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Carbon–silica sol-gel derived nanomaterials

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The preparation of sol-gel derived silica-based nanomaterials containing electrical conductive carbon fillers in an extensive composition range is described and their electrical properties are presented. Nanomaterials of carbon filler concentrations up to 60% (v/v) were obtained by dip coating or screen-printing from precursors of hydrolysed alkoxysilanes. Nanostructured morphology could be identified to consist of homogeneously dispersed carbon black particles or carbon fibres of 30 to 500 nm in size in a modified silica matrix. The electrical resistivity of the films changes drastically from 10^{10} to 10^{-1} Ω·cm, according to the amount of dispersed conductive particles. A threshold between 5 and 50% (v/v), at which the resistance abruptly decreases, was determined. A geometrical model related to percolation theory explains this non-linear dependence on the filler composition in the materials. Moreover the temperature dependence of resistance and the current-voltage characteristics of the nanomaterials can also be illustrated using this geometric model.

Key words: *sol-gel, nanomaterials; carbon black; electrical resitivity; percolation*

1. Introduction

Silica materials prepared by the sol-gel route combine excellent chemical and temperature stabilities with a high electrical resistance (above 10^{15} Ω·cm) [1]. The addition of conductive fillers into the insulating matrix may result in a change of its properties and reduction of the resistance, which can offer new applications. The synthesis of sol-gel films containing fine noble metal particles such as gold or platinum is already known to optical applications [2]. The addition of silver or cupper oxide is proposed for optical or antibacterial use [3–5]. The formation of other metals in a glass matrix, like nickel or cobalt, demands an additional reduction process employing hydrogen gas at higher temperatures [6]. We chose carbon black as a cost-effective material, which should be introduced into the sol-gel matrix at high concentrations. Carbon black shows a low resistivity (about 10^{-5} Ω·cm) and is stable under

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the oxidizing conditions of film preparation. Various kinds of carbon black are industrially produced for several applications. The single particles are mostly nanosized, but as in many other nanopowders they tend to agglomerate and form larger aggregates.

Carbon organic polymer composite materials, such as films or compact materials, have been widely studied and applied, for example, in rubber material or duro plastics for electronic units, conductive glue, anti-electrical charging, and electrical shielding. The dependence of electrical properties on carbon black concentration have already been well studied [7–9]. Inorganic or hybrid sol-gel derived materials containing carbon black in a silica matrix are already used in applications such as biosensors and electrodes for electrochemical and analytical procedures as so-called carbon containing electrodes (CCE) [10–12]. The resistance of the composite materials is related to the formation of a network of contacting filler particles within the matrix. It decreases sharply at a characteristic conducting particle concentration, known as the percolation threshold [13]. On the other hand, systematic investigations of materials containing carbon embedded in an inorganic or hybride matrix prepared by wet synthesis are still incomplete [13]. Therefore, in this study, modified silica nanomaterials containing different kinds of carbon black or carbon nanofibres were synthesised via the sol-gel process and their morphology and electrical properties were characterised. Films in a wide range of filler concentrations were prepared and examined. Preparation includes a traditional dip-coating process, so that crack-free films with a thickness smaller than 10 μm can be obtained. In order to obtain thicker films, silk screen printing was applied, which demands an increased viscosity of the usual liquid precursor. Therefore, other compositions had to be considered and further additives were neccessary.

2. Experimental

2.1. Synthesis of films

Precursor solutions for thin films were obtained from a mixture of tetraethoxysilane (TEOS), methyltriethoxysilane (MTES), water, and ethanol, in a molar ratio of 0.67:1:0.9:2.6, which was heated at 40 °C for 4 h. Hydrolysis was catalysed by 0.01 M HNO_3. An alcoholic solution of 20% graphite was added in order to obtain 5–60% (v/v) carbon in the completed films. Silicon wafers, fused silica, and silicate glass were used as substrate materials. Employing a dip-coater, the substrates were dipped into the precursor solution mixture and withdrawn at rates between 3 and 25 $cm \cdot min^{-1}$. The films were dried for an hour at 50 °C and for 4 hours at 100 °C, followed by heat treatment at 450 °C for 20 min. The heating rate was 1 $K \cdot min^{-1}$. The basic solution was stable for more than 90 days without any relevant increase in particle size and viscosity, which was tested by light scattering experiments and viscosity measurements.

Thick films were obtained from a mixture of tetraethoxysilane (TEOS), glycidyloxypropyltrimethoxysilane (GPTS), 3-methacryloxypropyltrimethoxysilane (MPTS), diphenyl-silandiol (DPS), and water in the molar ratio 1: 9.75:9.75:4.5:13.38. In order to increase the viscosity of the precursor, up to 10% silica (Degussa, Aerosil® R972) or a modified silicate (Southern Clay Prod. Inc., Cloisite B30) was added. Four different carbon black powders (Degussa, XE-2B and L6, and RUF IN-1, IN-2) and carbon nanofibres (Applied Sciences INC., Pyrograf III) were added in concentrations up to 20% to the paste and homogenised using an ultrasound stick or bath (Bandelin). The paste was printed on alumina and glass substrates and heat-treated up to 200 °C for 15 min.

2.2. Material characterization

The thickness of the films was determined by a mechanical stylus system (Tencor Instr., Alpha-Step 200). SEM investigations (Hitachi S4100) were performed for characterising the morphology of the carbon and of the prepared filled nanomaterials on cuts perpendicular to the coated substrate. The electrical resistance of the films was measured by an I–V measurement system (Material Development Corp.), which uses electrodes consisting of a mercury dot (760 μm in diameter) surrounded by a mercury ring. Samples of different filler content were investigated with d.c. and a.c. up to the frequency of 1 MHz. The specific resistance was calculated from the measured sheet resistance and film thickness. The temperature dependence of resistance was investigated within the range from –30 to 150 °C. The temperature coefficient of resistance (TCR) was calculated from the slope of the least-squares regression line.

3. Results and discussion

The SEM investigation shows that the carbon black fillers vary in their grain sizes from 30 to 500 nm. The carbon fibres have diameters of 70–300 nm and lengths of 30–150 μm (Fig. 1). The micrographs indicate that the most carbon black particles are homogenously dispersed in the sol-gel derived modified silica matrix. Although the sol was treated by ultra sound for homogenisation, carbon black forms aggregates with a diameter of 200–800 nm in the SiO_2 matrix. The thickness of the films prepared by dip coating was 0.3–3 μm, depending on the filler concentration and rate of withdrawal. The layers prepared by screen-printing have the thickness of 10–30 μm. Both types of films exhibit good mechanical stability and adhesion on the substrate.

The films with high filler content show linear current–voltage characteristics in d.c. measurements, whereas in the case of low carbon black filler concentrations a non-linear behaviour was observed, which is typical of semiconductive materials (Fig. 2). For interpreting this behaviour, a model of two kinds of geometrical arrangements of adjacent conductive particles in the insulating matrix is used [15]. In the first type of arrangement, the particles contact each other directly while in the

other one the particles are separated by a very thin insulating layer and form a metal –insulator–metal unit. At low filler concentrations, most clusters form the latter type of arrangement, so that conductivity occurs via a tunnelling effect, which can explain the non-ohmic behaviour. At high filler concentrations contacting particles prevail and an ohmic-type of conductive mechanism dominates.

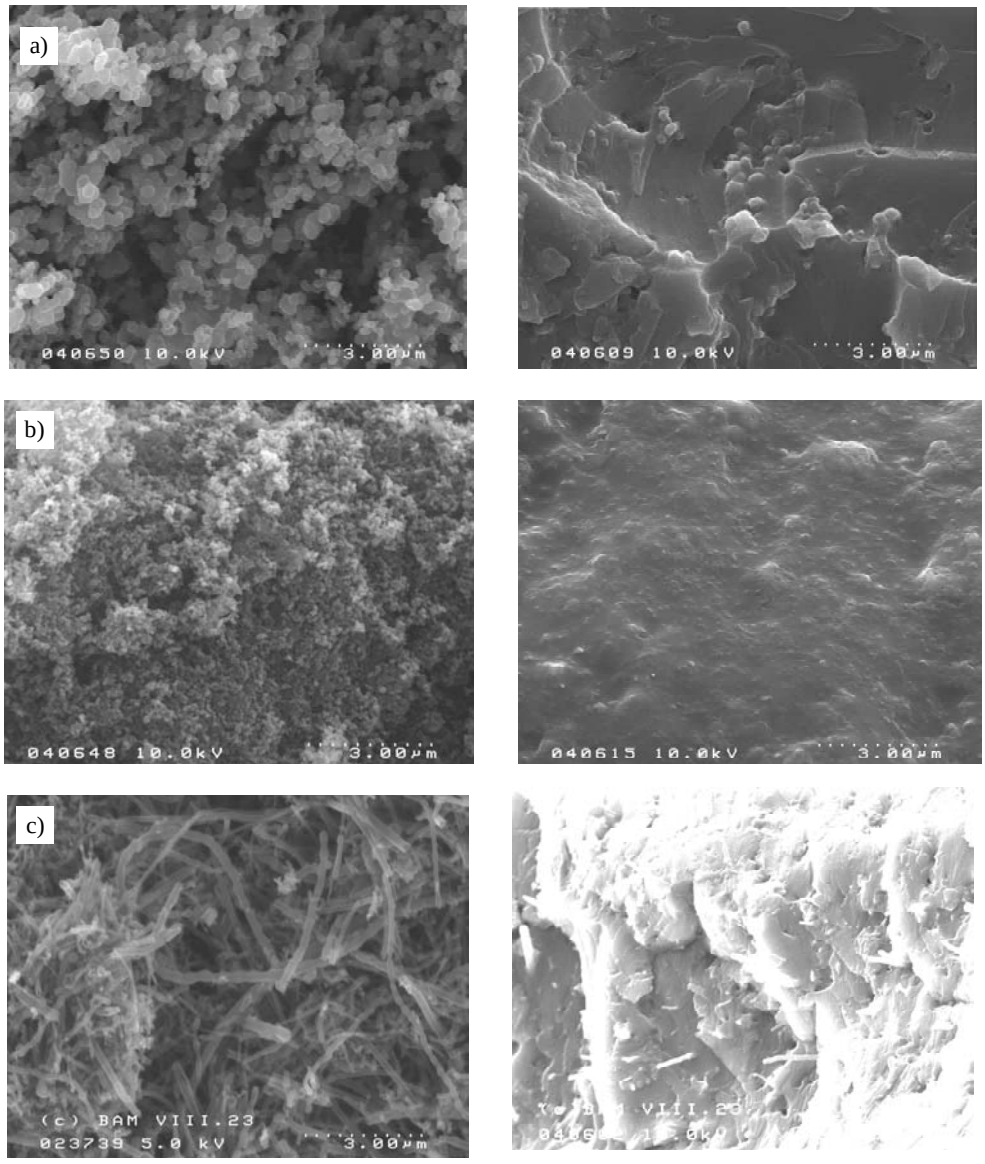

Fig. 1. SEM photomicrographs of various carbon fillers (left side) and the corresponding sol-gel derived thick films (right side), containing 5% (v/v) C: a) IN-1, b) 2B, c) Pyrograf III

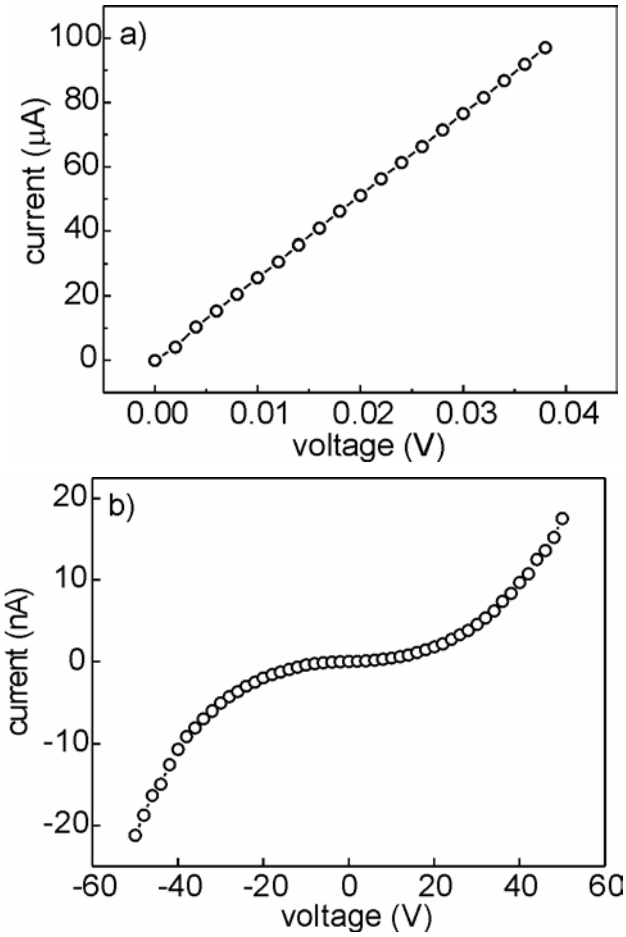

Fig. 2. Current–voltage characteristics of thin modified silica films containing carbon black: a) SiO_2 50% (v/v) C, b) SiO_2 60% (v/v) C

The resistivity of the films depends on the filler concentration in a characteristic manner. Although the carbon black concentration increases, the films have a high resistivity up to a critical filler concentration. Around the critical concentration, the resistivity drops drastically and reaches a minimum value. The resistance of thin films prepared by dip-coating remains nearly unaffected up to a carbon black concentration of about 50% (v/v), and then decreases abruptly. A detailed investigation of the influence of the amount of carbon black amount on resistivity gives the results shown in Fig. 3 [16].

This non-linear behaviour can be explained by the percolation theory. Fine conductive particles are dispersed in an insulating matrix and build agglomerates, so-called clusters. It is assumed that electric current can flow between particles being nearest neighbours. When a cluster spans the system from one side to the other (from one electrode to the other) at a concentration v_c, the so-called percolation threshold,

then the properties of the system change drastically from insulating to semi-conducting and conducting. The percolation transition is a critical phenomenon and implies that physical quantities related to the transition can be characterised by power laws of $(v - v_c)$:

$$R = K(v - v_c)^{-\beta} \tag{1}$$

Here R is resistivity, K and β are constants, v is the concentration of the conducting particles, and v_c the critical concentration. For thin films prepared by dip-coating, the most appropriate curve can be obtained for K = 0.03, β =1.75, and v_c = 0.50. This means that the electrical path of clusters is built at a filler concentration of 50% (v/v). The percolation threshold is strongly influenced by particle size and morphology. Typically values of 4–12 % (v/v) [17], but also up to 35 % (v/v) [9] and even below 0.2 % (v/v) [7] have been reported. The estimated relatively high value of v_c =0.50 indicates particle aggregation. The value of the critical exponent β between 1.3 and 1.75 was observed for a two-dimentional percolation network, which is supposed from the theory, and 2 for a three-dimensional model [18, 19].

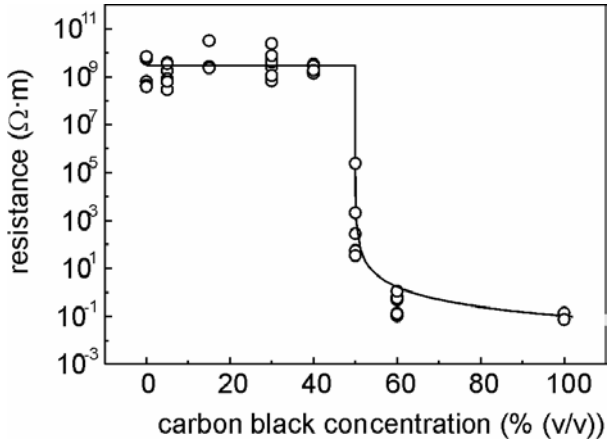

Fig. 3. The percolation threshold of a thin film material

The resistivity of films prepared by screen-printing changes from 10^9 to 1.0 Ω·cm at a critical concentration of about 5% (v/v). The influence of grain size can be observed. Films containing various kinds of carbon fillers differ in the minimum resistivity. Those including carbon black with particle diameter of about 500 nm, carbon fibre, and carbon black of finer grain size exhibit a minimum resistivity of 10^8, 10^4 and 1.0 Ω·cm, respectively (Fig. 1). Although the carbon particles in the graphite paste used to prepare thin films are smaller than most of those in the solution used to prepare thick films, they built aggregates and behave similarly to larger particles in the sol. These secondary particles make the percolation threshold of dip-coating films produced by graphite solution higher than of screen-printed films.

The dependence of the film resistance on frequency was determined in the range from 20 Hz to 1 MHz. The resistivity of the films showing high resistivity (above $10^3\,\Omega\cdot$cm) at 20 Hz decreases with increasing frequency linearly in a logaritmic scale, whereas films of low resistivity (below $10^2\,\Omega\cdot$cm) at 20 Hz are nearly independent on frequency until 1MHz. This behaviour could be illustrated by the tunnel effect. It is assumed that the current between clusters (agglomerations of conducting particles), which are separated by a very thin insulating silica layer, occurs by means of the tunnelling effect. The resistivity of a film can then be found from the tunnelling current using the following equation

$$\rho_{AC} \propto \frac{1}{\sigma_0 + 2\pi f \varepsilon_0 \varepsilon''} \tag{2}$$

Here σ_0 is the part of the conductivity that is not influenced by the frequency *f*, ε_0 is the permittivity of vacuum and ε_r'' the loss index. At low carbon filler amounts, the films show higher resistivity and the term $2\pi f \varepsilon_0 \varepsilon_r''$ is significant, which results in a strong frequency dependence of the resistance for highly resistant films. Above the percolation threshold, σ_0 dominates and the impedance values are less influenced by the frequency.

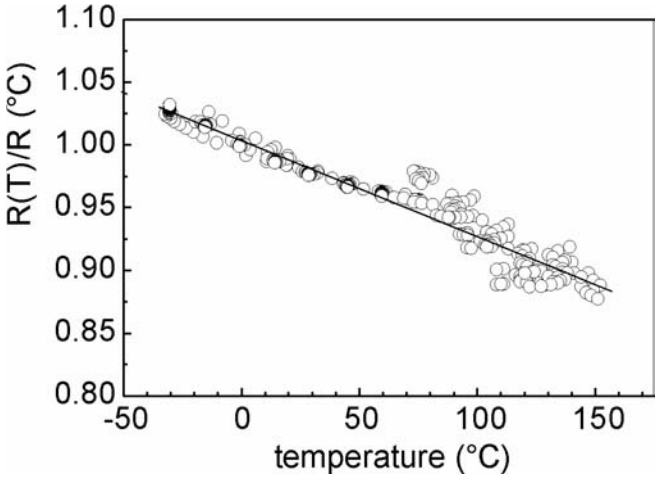

Fig. 4. The temperature dependence of the resistance of modified silica films containing 60% (v/v) carbon black at 1 kHz; TCR = -760×10^{-6} K^{-1}, uncertainty $\pm10\times10^{-6}$ K^{-1}

Measurements of the temperature dependence of resistance between –30 and 150 °C give a negative temperature coefficient of resistance (TCR) for both types of films. An example for a thin film is given in Fig. 4. Depending on the film composition, the TCR varies from –200 to -1300×10^{-6} K^{-1}, which is comparable to values of carbon-based resistors.

4. Conclusions

Nanocomposites containing carbon fillers in a wide composition range can be prepared via the sol-gel process. The variation of filler concentration and grain size results in changes in resistance and its dependence on voltage and temperature. This behaviour is not immediately related to the concentration of the components and their mixture, but can be illustrated using the percolation model and a specific conductive mechanism of two kinds of adjacent small conductive particles. These nanomaterials can be considered to be promising new functional materials for miniaturized resistor units, electrodes, and sensors, combining interesting electrical and improved mechanical and thermal properties.

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